

soluble and energetic than the same amount contained in porous phosphatic materials, such as certain descriptions of phosphoguanos.

6. Treatment with acids renders the material completely soluble in water, and the so-formed superphosphate, when put into the ground, is precipitated in a very fine state of division.

7. In the precipitated state the insoluble phosphate is immeasurably more finely divided than it could be obtained by mechanical means, and is consequently more energetic than any raw material mechanically ground.

8. The author's conclusion is that the chemical treatment with acid is the cheapest and best way of rendering mineral phosphates useful for agricultural purposes.

We think that it will be generally admitted that these propositions give a very reasonable statement of the case; but for the purposes of our inquiry we must supplement them with the following additional proposition. This has reference to a matter which has escaped the attention of Dr. Voelcker, but which is strongly supported by the results of the numerous recently-recorded practical trials.

"By reprecipitating the acid in a super-phosphate previous to its employment for agriculture by means of a suitable base, it becomes possible to obtain a neutral phosphate, possessed of a sufficient degree of solubility to be readily distributed through the soil, in an extremely fine state of subdivision, and capable of affording nutriment to the plant under highly favourable conditions."

It is to this further proposition to which we now desire to call special attention, and we may allude first to the assumed loss of the power of spontaneous diffusion through the soil, which is stated by Sibson, in his work on "Artificial Manures," to render the precipitated phosphates inferior in value to soluble acid phosphate. We think that no chemist will doubt that the phosphates in guano are sufficiently soluble to be available for plant food, and precipitated phosphate is certainly more soluble than the earthy phosphates in Peruvian guano. It must be remembered, moreover, when studying the table of solubilities of phosphates, as ascertained by Dr. Voelcker, that these are stated with reference to distilled water, which does not occur in nature, whereas in water containing small percentages of many of the salts, commonly present in the soil, the solubility of phosphates is largely increased. Thus the addition to the water of a trifling amount of ammoniac chloride (1 per cent.) increases the solubility of precipitated calcic phosphate fourfold.

This matter has not then received a due share of attention, for, as we have seen, arguing on the analogy of guano, phosphates, in the precipitated form, are undoubtedly so far soluble as to possess the power of diffusion to an extent amply sufficient for agricultural purposes, and there must be a point, short of perfect solubility, which adequately satisfies all requirements in this respect. A careful consideration of the subject has led us to the conclusion that the effect of phosphoric acid added to the soil, after having been fixed by a suitable base, in a condition sufficiently soluble for every need of the plant, and in a state of subdivision far finer than anything which could be obtained by mechanical means, would be in theory, if not superior, at least equal to that of a similar amount of soluble phosphate, applied to a soil promiscuously, in cases in which it is impossible to predict by what bases the phosphoric acid will be fixed, or even whether it will be fixed at all. Indeed, the foregoing considerations would almost lead us to the belief that the employment of such ready-formed compounds as calcic or magnesian phosphates would be preferable to the haphazard use of soluble phosphoric acid in a super-phosphate.

Chemists in treating of the magnesian phosphates appear to have overlooked the dibasic phosphate and to have conducted their experiments and to have founded their observations mainly, if not entirely, on the behaviour of the far less soluble tribasic phosphate. The freshly-precipitated magnesian phosphate is soluble in about 322 times its weight of pure water, while calcic phosphate, as we have seen when newly precipitated, is soluble to the extent of 5.56 grains per gallon. Both of these salts are therefore much more soluble than the earthy phosphates present in guano. We must not overlook the fact also that although it has not yet received much attention, the magnesia would appear to possess in itself considerable manurial value. A recent French authority assigns to it a value approaching 5s. 8d. per unit, almost three-fourths of the price he sets down for phosphoric acid, and we are convinced from the study of the composition of numerous fertile soils, the ashes of plants, and

recent field-trials, that the day is not far distant when the magnesia will rank as high in a manure as a salt of potash.

Another fact which the foregoing considerations have forcibly brought before us is the value of organic matters, in bringing about the solubility of the phosphates. This is perhaps scarcely within our present scope, but we have mentioned, incidentally, that small quantities of ammonia and carbonic acid, dissolved in the water, produce a very marked effect on the solubility of the phosphates. So valuable is their office in this respect, that it seems a false system to deny that organic matter, when present in a manure, possesses any value whatever. It was formerly the practice with agricultural chemists to allow 1*l.* per ton (2.4*l.* per unit) for organic matter, and we think that the important office which it fulfils in supplying carbonic acid for bringing into solution additional quantities of the phosphates, fully justifies the assignment to it of the above valuation.

We have thus endeavoured to explain the true conditions under which phosphoric acid becomes, in the soil, a source of plant-food. We have shown that there must be a limit to the value of solubility, merely considered as a means of securing diffusion through the soil, because partially soluble salts also possess the property to a degree sufficient for all practical purposes. In conclusion we have claimed for a ready-formed, partially-soluble phosphate, in a finely divided condition, and, in the case of the magnesian phosphate, possessing the property of fixing at the same time a portion of the ammonia, a value at least as great as that of a soluble acid phosphate, which runs the risk of being fixed by iron, or alumina (should lime be deficient in the soil), or, which may sink below the roots of the plants before it is neutralised. We trust we have thus shown a good case for a more liberal valuation of precipitated phosphates, and have indicated, with some measure of success, the reasons for the excellent results that have been recently obtained by the use of manures containing phosphoric acid in this form.

#### THE ELECTROLYTIC BALANCE OF CHEMICAL CORROSION<sup>1</sup>

THIS paper treats of some fundamental points in silver electroplating, and shows how a large amount of the electric power may be wasted by the use of too large a proportion of free potassic cyanide in the plating-solution, or by using the liquid in a heated state.

It is also described a method of ascertaining the degree of energy of chemical corrosion of metals in electrolytes, by means of the strength of electric current per unit of surface necessary to prevent such corrosion; the metals and liquids employed for the purpose in the present research being silver, and solutions of argento cyanide of potassium containing free potassic cyanide. Numerous examples, chiefly in the form of tables, are given of the strength of current required to enter cathodes of a given amount of surface, in order to exactly balance the chemical corrosive effect upon them at atmospheric temperatures, and at higher ones, of solutions of potassic cyanide of various degrees of strength.

The method employed was to take a given solution of cyanide of potassium, pass through it by means of a sheet of platinum anode and a burnished sheet of silver cathode, a weak electric current, and add gradually to the liquid (with stirring) small portions of argento potassic cyanide, until the faintest perceptible deposit of silver occurred. The verge of deposition thus attained was called "the balance point;" and the conditions which determine and influence it, constitute the subject of this research.

The effect of various conditions upon the point of balance of electric and chemical energy were investigated, and the experiments are described. The influences examined were: composition of the liquid, strength of current, size of cathode and density of current, electro-motive force, temperature, ordinary chemical corrosion, nature of the cathode, etc. The circumstances were also investigated which affect the measurement of the current by the method employed in this research, viz. by depositing silver from a solution of argento potassic cyanide; and the sources of error, (and their limit), in that method, are pointed out. The effect of varying the proportions of free potassic cyanide, and of argento potassic cyanide, upon the strength of current at the balance point, are shown in tables of results. The strengths of current just sufficient to prevent all

<sup>1</sup> Abstract of paper by G. Gore LL.D., F.R.S., read before the Birmingham Philosophical Society, Dec. 14, 1882.

corrosion and to deposit the whole of the silver from a solution of argento potassic cyanide of given composition and containing free cyanide are also shown. The influence of varying the proportions both of argento potassic cyanide, and free cyanide of potassium, upon the transfer resistance<sup>1</sup> of the solution, and thereby upon the balance point, are also investigated and the results described.

A number of results and conclusions were arrived at, some of which are as follows:—variation either of the number of battery elements, the proportion of water, of free potassic cyanide, or of argento potassic cyanide, destroys the balance. The effect of altering the proportion of water is opposite with strong solutions to what it is with weak ones. The electric current at the point of balance appears to be entirely conveyed by the free potassic cyanide, and does not divide itself between the two salts until the liquid contains a certain proportion of argentic salt. In strong solutions of potassic cyanide, decreasing the number of battery cells, necessitates more cyanide of silver to restore the balance. The alteration of the point of balance by alteration of proportion of free potassic cyanide cannot be much accounted for by alteration of corrosive power of the liquid. A current from ten Smee's elements is about sufficiently strong to prevent all corrosion of silver at 60° F. in a solution of cyanide of potassium containing a mere trace of argento potassic cyanide. The addition of nitrate, chloride, iodide, or sulphate of potassium to the cyanide solution has but little effect upon the balance point. Variation of strength and of "density" of current affect greatly the point of balance. Greater "density" irrespective of strength of current usually increases the amount of silver deposited. Difference of electro-motive force of current had no conspicuous effect in altering the balance point. Rise of temperature of the liquid acts in two opposite ways, it increases the corrosive action, and by diminishing conduction-resistance it increases the current, and as the latter effect is usually a little stronger than the former one, rise of temperature alters slightly the point of balance, and enables the current to produce a sparing deposit of silver. The ordinary chemical corrosion of silver in a solution of potassic cyanide without an electric current is increased slightly by partial immersion (through capillary corrosion), and greatly by rise of temperature; it is also slightly greater in a weak solution than in a strong one, with solutions of a certain range of strength; and it is distinctly increased by contact with platinum. In consequence of the latter circumstance, a platinum cathode requires a somewhat stronger current than a silver one to enable the point of balance to be attained. In a mixed solution of potassic and argento potassic cyanides, even the smallest proportion of the former salt conveys a portion of the current, and if the cathode is large or the current is sufficiently weak, the whole of it is conveyed by that salt, however much of the double salt is present, an error is thereby introduced when deposition of silver in such a liquid is used as a measure of current. But with a large amount of the double salt, a small amount of potassic cyanide, and a current sufficiently strong, the proportionate amount of error is small. During the act of deposition the cathode surface is not at all corroded, and any deficiency in the weight of deposit is not due to corrosion, but to a portion of the current being conveyed by other ingredients of the liquid than the argentic salt. A current which produces deposition of silver, prevents all corrosion of a silver cathode in the same liquid. The addition of free potassic cyanide to a solution of the double cyanide alters both the resistance and the balance point. The quantity of current diverted from the argentic salt in solution is directly proportional to the amount of free potassic cyanide present, but not always in the same ratio. The presence of a large proportion of free cyanide, together with the employment of a feeble current conduce to the passage of a large amount of current through the liquid without depositing silver; and a current of '001057 Ampere (which would deposit '132 grain of silver in two hours) was hardly strong enough to prevent all corrosion or to deposit any silver from a solution composed of 37·5 grains of argento potassic cyanide and 112·5 grains of free cyanide of potassium in three ounces of water. Whilst also a current if sufficiently weak, may traverse a solution of potassic cyanide containing double cyanide, without any of the current decomposing the latter, it cannot traverse a solution of double salt containing free potassic cyanide without some of it traversing the cyanide of potassium.

With a very dense current also, a portion of it enters the cathode without depositing silver, and evolves gas.

It requires a much stronger current to balance the corrosion in a hot solution of the two cyanides than in a cold one, and in an instance given, a rise of temperature from 60 to 120° F. was attended by the passage of 21 per cent increase of current without deposition of silver. Addition of free potassic cyanide to a weak solution of the double salt *at the balance point*, first decreases and then increases the current by altering the transfer resistance, probably at the cathode. An amount of current equal to '14857 Ampere, entering a surface of  $\frac{3}{8}$ ths. of a square inch, was found to be sufficiently strong to deposit nearly the whole of the silver from a solution at 60° F. composed of 70·11 grains of free potassic cyanide, '0297 grain of double cyanide, and three ounces of water, the liquid retaining dissolved a little less than that amount of silver at its balance point under those conditions. The strength of current *at the balance point* in a weak solution of potassic cyanide, varies inversely as the amount of silver salt added, and at about eight times the rate. A certain strength of current must enter a given surface of silver in a given liquid under stated conditions in order to prevent all corrosion and produce deposition. The addition of the double cyanide reduces the amount of current conveyed by the free potassic cyanide into the cathode *at the balance point*. Successive additions of double salt to a solution of potassic cyanide *not at the balance point*, first decreases and then increases the current by altering the transfer resistance; it alters the relation of the molecules of potassic cyanide to the cathode so as to diminish their power of transmitting current into that surface without depositing silver. The greater the proportion of double salt present, the greater the tendency to the deposition of silver. Addition of potassic cyanide to a weak solution of the double salt *not at the balance point*, first decreases and then increases the current by altering the transfer resistance at the cathode; in this respect it behaves like addition of the double salt to a weak solution of potassic cyanide. With cathodes of platinum, a solution of potassic cyanide offered less resistance to the current (*not at the balance point*) than one of the double cyanide, but with silver cathodes the reverse effect occurred.

The balance point is a case of equalization of molecular influences, including ordinary chemical corrosion, density of current, nature of cathode, temperature, proportions of water, argento potassic cyanide, free potassic cyanide, and the soluble salts present as impurities, either of which by being disturbed, alters all the others. All these influences also have separate numerical values. A rise of temperature of 60° F. requires an increase of '000976 Ampere to restore the equipoise. The experiments illustrate the dynamics of electro-silver plating; and the method employed in the research is applicable to the detection and measurement of molecular influence in electrolytes. In consequence of the alteration of any one of the conditions having the effect of altering all the remainder, all the above conclusions are limited in their application and are only correct under the conditions given in the paper. The fundamental explanation underlying these conclusions is, that the phenomena are essentially molecular; and that the mere presence and admixture of the double cyanide alters the molecular arrangement of the free cyanide *not at the balance point*, in such a way as to enable the latter to transmit a greater quantity of current into a cathode of given size, notwithstanding its being more diluted by the other salt.

The phenomena of the "balance point" constitute an interesting example of molecular equilibrium, in which the balance point may be compared to a ball suspended by an elastic cord, and having attached to it, a number of other similar cords, each drawing it in a different direction, and all of them being kept in a state of tension. In such a case an alteration of the degree of strain of any one of the cords, changes that of all others, and alters the position of the ball.

The research has a practical bearing both upon the measurement of electric currents by means of deposition of silver from a cyanide solution, and upon the technical process of electro plating. In the former it shows how a large proportion, or even the whole of a current may pass without being measured, and how the error may be reduced to the smallest amount; and in the latter, how a similar waste of current may occur, and how to prevent it.

It is manifest from the foregoing research, that the electrolytic balance of chemical corrosion of cathodes in other depositing solutions, such as those of gold, copper, nickel, etc., might form an extensive subject of experimental investigation.

<sup>1</sup> By transfer resistance is meant the resistance to transfer of the current into the cathode.



*Appended Note.*—It was constantly found that in using a non-corrodible anode such as platinum, the amount of current passing was very much more easily regulated by varying the size of the anode than that of the cathode, with a corrodible anode however, such as silver, this effect was not observed.

## THE ETHER AND ITS FUNCTIONS<sup>1</sup>

### II.

Consider the effect of wind on sound. Sound is travelling through the air at a certain definite rate depending simply on the average speed of the atoms in their excursions, and the rate at which they therefore pass the knocks on; if there is a wind carrying all the atoms bodily in one direction, naturally the sound will travel quicker in that direction than in the opposite. Sound travels quicker with the wind than against it. Now is it the same with light: does it too travel quicker with the wind? Well that altogether depends on whether the ether is blowing along as well as the air; if it is, then its motion must help the light on a little; but if the ether is at rest no motion of air or matter of any kind can make any difference. But according to Fresnel's hypothesis it is not wholly at rest nor wholly in motion; the free is at rest, the bound is in motion; and therefore the speed of light with the wind should be increased by an addition of  $(1 - \frac{1}{\mu^2})$ th of the velocity of the wind. Utterly infinitesimal,

of course, in the case of air, whose  $\mu$  is but a trifle greater than 1; but for water the fraction is 7-16ths, and Fizeau thought this not quite hopeless to look for. He accordingly devised a beautiful experiment, executed it successfully, and proved that when light travels with a stream of water, 7-16ths of the velocity of the water must be added to the velocity of the light, and when it travels against the stream the same quantity must be subtracted, to get the true resultant velocity.

Arago suggested another experiment. When light passes through a prism, it is bent out of its course by reason of its diminished velocity inside the glass, and the refraction is strictly dependent on the retardation; now suppose a prism carried rapidly forward through space, say at the rate of eighteen miles a second by the earth in its orbit, which is the quickest accessible carriage; if the ether is streaming freely through the glass, light passing through will be less retarded when going with the ether than when going against it, and hence the bending will be different.

Maxwell tried the experiment in a very perfect form, but found no difference. If all the ether were free there would have been a difference; if all the ether were bound to the glass there would have been a difference the other way; but according to Fresnel's hypothesis there should be no difference, because according to it, the free ether, which is the portion in relative motion, has nothing to do with the refraction; it is the addition of the bound ether which causes the refraction, and this part is stationary relatively to the glass, and is not streaming through it at all. Hence the refraction is the same whether the prism be at rest or in motion through space.

An atom imbedded in ether is vibrating and sending out waves in all directions; the length of the wave depends on the period of the vibration, and different lengths of wave produce the different colour sensations. Now through free ether all kinds of waves appear to travel at the same rate; not so through bound ether; inside matter the short waves are more retarded than the long, and hence the different sizes of waves can be sorted out by a prism. Now a free atom has its own definite period of vibration, like a tuning-fork has, and accordingly sends out light of a certain definite colour or of a few definite colours, just as a tuning-fork emits sound of a certain definite pitch or of a few different pitches called harmonics. By the pitch of the sound it is easy to calculate the rate of vibration of the fork; by the colour of the light one can determine the rate of vibration of the atom.

When we speak of the atoms vibrating, we do not mean that they are wagging to and fro as a whole, but that they are crimping themselves, that they are vibrating as a tuning-fork or a bell vibrates; we know this because it is easy to make the free atoms of a gas vibrate. It is only in the gaseous state, indeed, that we can study the rate of vibration of an atom; when they are packed closely together in a solid or liquid, they

are cramped, and all manner of secondary vibrations are induced. They then, no doubt, wag to and fro also, and in fact these constrained vibrations are executed in every variety, and the simple periodicity of the free atom is lost.

To study the free atoms we take a gas—the rarer the better—heat it, and then sort out the waves it produces in the ether by putting a triangular prism of bound ether in their path.

Why the bound ether retards different waves differently, or disperses the light, is quite unknown. It is not easy accurately to explain refraction, but it is extremely difficult to explain dispersion. However, the fact is undoubted, and more light will doubtless soon fall upon its theory.

The result of the prismatic analysis is to prove that every atom of matter has its own definite rate of vibration, as a bell has; it may emit several colours or only one, and the number it emits may depend upon how much it is struck (or heated), but those it can emit are a perfectly definite selection, and depend in no way on the previous history of the atom. Every free atom of sodium, for instance, vibrates in the same way, and has always vibrated in the same way, whatever other element it may have been at intervals combined with, and whether it exists in the sun or in the earth, or in the most distant star. The same is true of every other kind of matter, each has its own mode of vibration which nothing changes; and hence has arisen a new chemical analysis, wherein substances are detected simply by observing the rate of vibration of their free atoms, a branch of physical chemistry called spectrum analysis.

The atoms are small bodies, and accordingly vibrate with inconceivable rapidity.

An atom of sodium vibrates  $5 \times 10^{14}$  times in a second; that is, it executes five hundred million complete vibrations in the millionth part of a second.

This is about a medium pace, and the waves it emits produce in the eye the sensation of a deep yellow.

$4 \times 10^{14}$  corresponds to red light,  $7 \times 10^{14}$  to blue.

An atom of hydrogen has three different periods, viz. 4'577, 6'179, and 6'973, each multiplied by the inevitable  $10^{14}$ .

Atoms may indeed vibrate more slowly than this, but the retina is not constructed so as to be sensible of slower vibrations; however, thanks to Capt. Abney, there are ways now of photographing the effect of much slower vibrations, and thus of making them indirectly visible; so we can now hope to observe the motion of atoms over a much greater range than the purely optical ones and so learn much more about them.

The distinction between free and bound ether is forced on our notice by other phenomena than those of light. When we come to electricity, we find that some kind of matter has more electricity associated with it than others, so that for a given electromotive force we get a greater electric displacement; that the electricity is, as it were, denser in some kinds of matter than in others. The density of electricity in space being 1, that inside matter is called  $\kappa$ , the specific inductive capacity. In optics the density of the ether inside matter was  $\mu^2$ . These numbers appear to be the same.

Is the ether electricity then? I do not say so, neither do I think that in that coarse statement lies the truth; but that they are connected there can be no doubt.

What I have to suggest is that positive and negative electricity together may make up the ether, or that the ether may be sheared by electromotive forces into positive and negative electricity. Transverse vibrations are carried on by shearing forces acting in matter which resists them, or which possesses rigidity. The bound ether inside a conductor has no rigidity; it cannot resist shear; such a body is opaque. Transparent bodies are those whose bound ether, when sheared, resists and springs back again; such bodies are dielectrics.

We have no direct way of exerting force upon ether at all; we can, however, act on it in a very indirect manner, for we have learnt how to arrange matter so as to cause it to exert the required shearing (or electromotive) force upon the ether associated with it. Continuous shearing force applied to the ether in metals produces a continuous and barely resisted stream of the two electricities in opposite directions, or a conduction current.

Continuous shearing force applied to the ether in transparent bodies produces an electric displacement accompanied by electric resilience, and thus all the phenomena of electric induction.

Some chemical compounds, consisting of binary molecules, distribute the bound ether of the molecule, at any rate as soon

<sup>1</sup> A lecture by Prof. Oliver Lodge at the London Institution, on December 28, 1882. Continued from p. 306.